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Photoelectric Investigation of the Surface Composition of Equilibrated Ag–Pd Alloys in Ultrahigh Vacuum and in the Presence of CO*

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Thin films of silver, palladium, and their alloys prepared by simultaneous sublimation onto Pyrex at 78 K and subsequently equilibrated at 573 K, were investigated by photoelectron emission to gain information on the surface composition by means of the work function (Φ) and the emission constant (*M*). The surface of films equilibrated in ultrahigh vacuum is found to be enriched with silver as can be expected on the basis of the difference in surface energy of Ag and Pd. In agreement with previous findings on the Au–Pt system, the Ag–Pd alloy surface becomes enriched with Pd upon prolonged contact with CO at 293 and 373 K. This process can be reversed by pumping CO at 573 K.

1. INTRODUCTION

The surface composition of equilibrated clean binary alloy films often differs vastly from the bulk composition. This has been proved convincingly for copper–nickel films equilibrated at 200°C (*1–3*). The surface composition of these alloys is constant and copper rich for various bulk compositions within the miscibility gap of the alloy system at 200°C, i.e., between about 25 and 98 atom% Ni. The original results of photoelectric investigations on Cu–Ni films (*1–2*) were repeatedly confirmed by other independent additional experiments such as the titration of the surface exposed Ni atoms with hydrogen (*4*), the kinetic data of the hydrogenation and deuteration of benzene (*3*), the recombination of H atoms on Cu–Ni foils (*5*) and by X-ray diffraction and electrical resistance measurements on Cu–Ni films used as catalysts for the decomposition of HCOOH (*6*).

As the miscibility gap of the Cu–Ni system is known to vanish at 322°C (*7*), Cu–Ni alloys equilibrated above this temperature do not show the phenomenon of constant surface composition. This consequence is in agreement with the catalytic data obtained by Zhavoronkova *et al.* (*8*) and by Byrne and Clarke (*9*) who used alloys equilibrated at 400 and 500°C, respectively.

The general principles used for interpreting the results on Cu–Ni alloys were also confirmed by results on the surface composition of Au–Pt alloy films (*10*). The latter system is comparable with Cu–Ni in that it fulfills the same conditions which are required for the peculiar phase separation of Cu–Ni alloys. Its phase diagram possesses a miscibility gap and one of the metals (viz., gold) is more mobile than the other metal.

On basis of the collected results on Cu–Ni and Au–Pt alloys, we may state that

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alloys characterized by a miscibility gap in the solid phase and consisting of metals having considerably different mobility will, under certain circumstances, have a surface composition which is constant for overall compositions within the miscibility gap of the alloy system.

However, the presence of two coexisting phases is not the only possible cause of differences in composition between surface and bulk. Also for single-phase alloys in ideal vacuum, thermodynamic equilibrium implies in general that the surface be enriched with that component which lowers the surface energy. If an adsorbing gas is present, the free energy of the system is further lowered by enriching the surface with that alloy partner which forms the strongest bonds with the adsorbate. Thermodynamics do not predict, however, whether either of these two effects will indeed be measurable at the very low temperatures—according to standards of metallurgy—where chemisorption is stable. Thermodynamic data are furthermore insufficient to predict the extent of segregation to be expected if indeed no kinetic limitations occur. It was therefore quite remarkable that we could show experimentally for Au–Pt alloys (*10*) that, at a temperature as low as 100°C, the surface becomes indeed enriched with one metal (in our case Pt) as a consequence of prolonged contact with a gas (CO) which forms relatively strong bonds with that metal and relatively weak bonds with the other metal. Even at room temperature, a slow aggregation of Pt in the surface could be detected. These results illustrate that metal atoms in and near the surface are relatively mobile. Under the influence of a gas which is chemisorbed strongly and probably corrosively by one of the metals (*11*), vacancies may be created in and near the surface. Pt atoms emerging at the surface are immediately fixed there by a chemisorbing CO-molecule. The irregular movement of the Pt and Au atoms thus becomes superseded by a preferred direction.

If our interpretation of these phenomena is correct, the implication would be that differences in composition between surface and interior should be observable in the absence and in the presence of an adsorbing gas also for those binary alloys which do *not* form two coexisting phases due to a miscibility gap. For ascertaining these phenomena, which are of considerable importance for the heterogeneous catalysis of alloys, it therefore appeared essential to study experimentally a binary alloy by preference of the Ib–VIIIb type which forms a continuous series of solid solutions within the temperature range of interest. The Ag–Pd system is one of the few binary alloy systems which fulfils this requirement (*12–14*) and which is attractive because the surface enrichment of one of the metals as a result of preferential chemisorption* can easily be studied on these alloys by using CO as the selective adsorbate. This gas is often chosen for adsorption studies and is well suited for our purpose of surface titration (*1–2*) because of its nondissociative adsorption.

As Ag has a lower surface tension than Pd, we expect that in vacuum the surface of clean equilibrated Ag-Pd films should contain more Ag than the underlying bulk. In analogy with our experiences on the Au–Pt system, we further expect that the surface of these equilibrated Ag–Pd alloy films will become enriched with Pd upon prolonged contact with CO because this molecule is chemisorbed relatively strongly by Pd but not by Ag under the conditions of temperature and pressure in the present work.

The films prepared were used as cathodes in photoelectron emission. The information gained in this way is expressed in terms of the work function (Φ) and the emission constant (M).

2. EXPERIMENTAL METHODS

The reader is referred to a previous article (*10*) for experimental details. The experiments were carried out in a photo-

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* We propose to call this phenomenon "chemisorption-induced aggregation," in contrast to "enrichment" in the case of the pure binary systems (alloys in ultrahigh vacuum).

tube described therein as tube II. Silver was evaporated from a multihairpin tungsten filament and Pd was evaporated as such. The alloy films, having an estimated thickness of 25–50 nm, were prepared by simultaneous sublimation of the two metals on the cathode support which was cooled at 78 K. After discontinuation of the sublimation process the film was equilibrated at 573 K during 16 hr. In order to ascertain that the films were properly equilibrated, annealing was repeated at the same and slightly higher temperatures; but no significant change of the emission data of the film was then detected. The overall composition of the alloy was calculated from the weight loss of the respective filaments and the geometric arrangement within the tube. Separate alloy films prepared under similar circumstances but in dispensable dummy cells were analyzed by X-ray diffraction for checking the homogeneity of the alloys and their calculated composition.

3. Results

The results are described in the following sections: (3.1) chemisorption of CO on equilibrated Ag and Pd films at 293 K; (3.2) chemisorption of CO on alloys at 293 K; (3.3) chemisorption-induced aggregation of alloy surfaces under the influence of CO at 293, 373, and 441 K.

3.1. *Chemisorption of CO by Equilibrated Ag and Pd Films at 293 K*

In a previous article (*15*) we have described experiments that indicate that the surface of thin metal films (thickness = 25–50 nm) can be equilibrated by heating for about 30 min at a temperature $T_s \cong 0.3\ T_m$ [T_m = melting point (K)]. These results originally derived from Au, Pt, and Ru films are confirmed for Ag and Pd films. As this simple expression seems to be also applicable for the equilibration of comparable alloy films, we can predict an estimated equilibration temperature of 500–600 K for the alloy films under study. Adsorption experiments with CO yielded the following results. On Ag no change of Φ and M was observed after admission of CO up to a pressure of 0.1 N m^{-2}*, which is in perfect agreement with recent findings by Bradshaw and Pritchard (*16*).

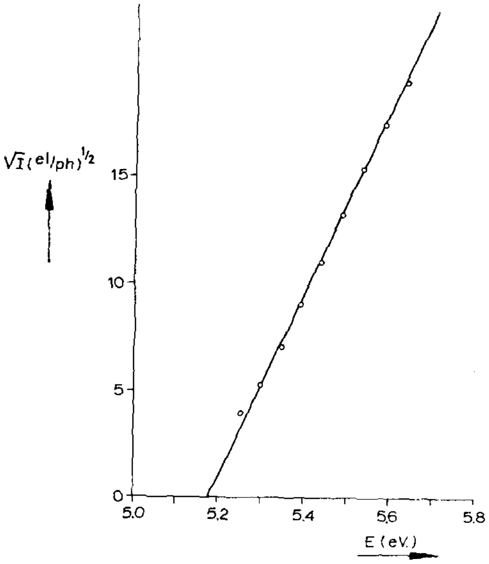

Fig. 1. Linearized Fowler plot of a clean Pd film (T_s = 573 K) before admission of CO.

On Pd, however, a behavior differing from that of all other group VIII metals studied so far was observed. Prior to admission of CO a linearized Fowler plot can be fitted to all data (Fig. 1). Immediately after admission of CO up to a pressure of 1.3 × 10^{-2} N m^{-2}, the original Fowler plot changes into a broken line apparently composed by superposition of

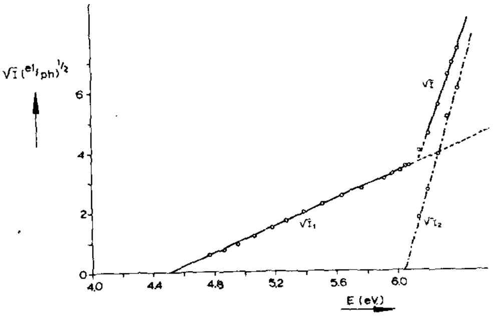

Fig. 2. Composite Fowler plot of a CO-covered Pd film (T_s = 573 K).

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* 1 Nm^{-2} = 7.501 × 10^{-3} Torr.

two straight lines (Fig. 2). These plots can be analyzed (*17*) yielding two distinct work functions Φ_I and Φ_2, respectively, as if there are two independently acting emission sources. After desorption by heating the film at 573 K while pumping off CO, a single linearized Fowler plot is again obtained (Fig. 3).

3.2. *Chemisorption of CO on Alloys at 293 K*

All further results of relevance for parts 3.2. and 3.3. are shown in Tables 1 and 2. The results on the work function and emission constant of the freshly deposited film after sintering at 293 K and after equilibration at 573 K, as well as immediately after admission of 1.3×10^{-2} N m^{-2} CO are shown in Figs. 4 and 5. It is noteworthy that after equilibration of the bimetal film by heating it at 573 K the work functions of all alloys are low and roughly equal to Φ_{Ag}. Immediately after admission of CO the work functions of all alloys are raised. The linearized Fowler plots of these alloys after short contact with CO are simple straight lines in contrast to the broken lines obtained with pure Pd under the same conditions.

In Fig. 6, the initial $\Delta\Phi$ values of the films after exposure to CO have been plotted as a function of the overall composition. For Pd, the higher of the two values derived from the broken Fowler line is used as its "fingerprint." We assume that this type of plot provides a reliable impression of the Ag content of the surface. In contrast to the results on the two-phase alloys Cu–Ni and Au–Pt, it can be seen that the Ag content in the surface of this one-phase alloy is not constant but decreases gradually with increasing Pd content of the bulk.

The behavior of the emission constant

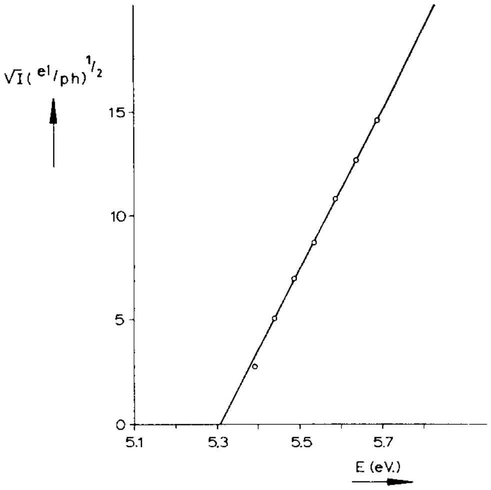

FIG. 3. Linearized Fowler plot of a CO-treated Pd film (T_s = 573 K) after desorption of CO at 573 K.

TABLE 1

THE WORK FUNCTION ϕ OF Ag, Pd, AND Ag–Pd ALLOY FILMS IN THE COURSE OF SUCCESSIVE TREATMENTS IN ULTRAHIGH VACUUM AND IN THE PRESENCE OF CO

Composition	Equilibration		Chemisorption of CO: at 293 K				at 373 K		Desorption
			Immediately after CO admission Φ(eV)		After 16 hr Φ(eV)		After 16 hr Φ(eV)		
x (at % Pd)	T_{eq} = 293 K	T_{eq} = 573 K	Φ_1	Φ_2	Φ_1	Φ_2	Φ_1	Φ_2	T_{des} = 573 K
0	4.33	4.38	4.38		4.38		4.38		4.38
10	4.36	4.37	4.46		4.45		4.45		4.37
17	4.36	4.36	4.53		4.45		4.45		4.40
33	4.38	4.44	4.53		4.56		4.50		4.44
53	4.41	4.52	4.78		4.51	4.85	4.51	4.89	4.52
72	4.50	4.50	4.82		4.51	4.90	4.51	5.09	4.52
86	4.87	4.50	4.84		4.51	4.92	4.50	5.18	4.51
100	5.11	5.22	4.50	6.04	4.50	6.04	4.50	6.04	5.33

TABLE 2

THE EMISSION CONSTANT M (10^{-12} ELECTRONS PHOTON^{-1} DEG^{-2}) OF Ag, Pd, AND Ag-Pd ALLOY FILMS IN THE COURSE OF SUCCESSIVE TREATMENTS IN ULTRAHIGH VACUUM AND IN THE PRESENCE OF CO

Composition	Equilibration		Chemisorption of CO: at 293 K				at 373 K		Desorption
			Immediately after CO admission		After 16 hr		After 16 hr		
x (at % Pd)	T_{eq} = 293 K	T_{eq} = 573 K	M_1	M_2	M_1	M_2	M_1	M_2	T_{des} = 573 K
0	11.4	9.8	9.8		9.8		9.8		9.8
10	18.8	5.0	6.9		6.2		6.5		6.7
17	23.9	6.0	5.8		5.8		7.4		5.0
33	29.4	4.8	3.8		3.5		3.5		4.7
53	33.4	11.2	12.5		0.25	14.0	0.34	10.4	14.8
72	37.9	22.1	20.8		0.14	20.0	0.09	15.2	22.7
86	42.5	31.6	25.1		0.12	21.4	0.06	17.1	25.1
100	51.9	28.1	0.07	1.17	0.07	1.17	0.07	1.17	23.7

M as a function of the overall composition is merely interesting from a phenomenological point of view. The shape of these curves (Fig. 5) is fairly reproducible. The absolute values of M are less so. The curves of M are smooth for the fresh vapor-quenched film after sintering at 293 K. Equilibration at 573 K causes a

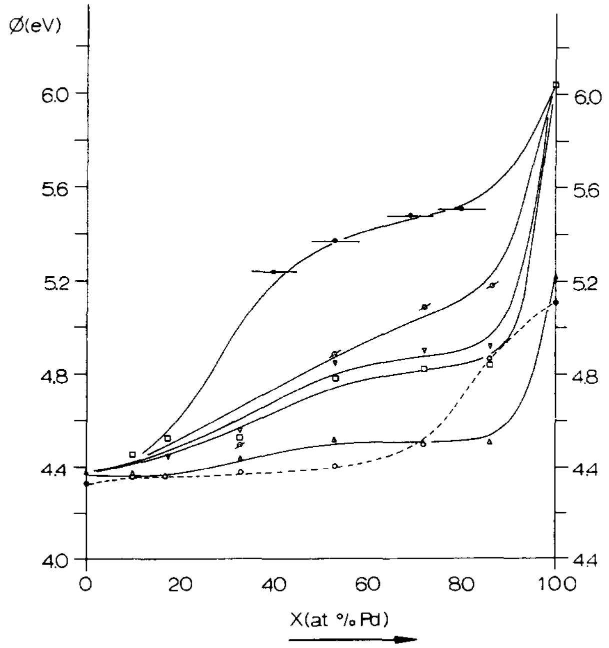

FIG. 4. Work function of Ag-Pd alloy films as a function of the overall composition: (○) freshly evaporated film; (△) equilibrated film; (□) immediately after admission of CO (p = 1.3 × 10^{-2} N m^{-2}); (▽) after 16 hr exposure to 1.3 × 10^{-2} N m^{-2} CO at 293 K; (⊙) after 16 hr exposure to 1.3 × 10^{-2} N m^{-2} CO at 373 K; (●) after 16 hr exposure to 1.3 × 10^{-2} N m^{-2} CO at 441 K. (These values originating from another Ag-Pd film are inserted although the overall composition is less accurate for this film.)

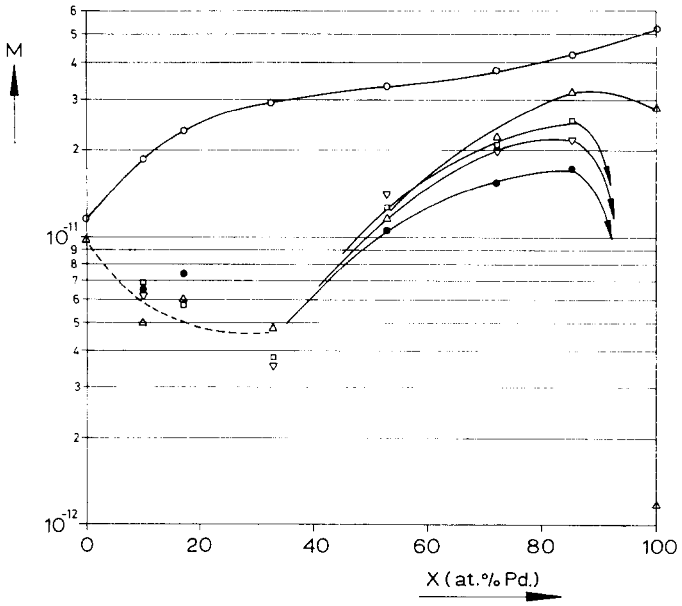

FIG. 5. The emission constant of Ag–Pd alloy films as a function of the overall composition: (○) freshly evaporated film; (△) equilibrated film; (□) immediately after admission of CO ($p = 1.3 \times 10^{-2}$ N m^{-2}); (△) after 16 hr exposure to 1.3×10^{-2} N m^{-2} CO at 293 K; (●) after 16 hr exposure to 1.3×10^{-2} N m^{-2} CO at 373 K.

relatively small reduction of M_{Ag} and M_{Pd} but a remarkable reduction of the emission constant of Ag-rich alloys.

M passes through a shallow maximum at 80–90 at % Pd. Immediately after admission of CO M_{Pd} is changed conspicuously while the emission constant of the Pd-rich alloys is affected only moderately. The values of the emission constant of Ag-rich alloys present a confusing picture. As it is known that the lattice constants of Ag–Pd alloys follow Végard's

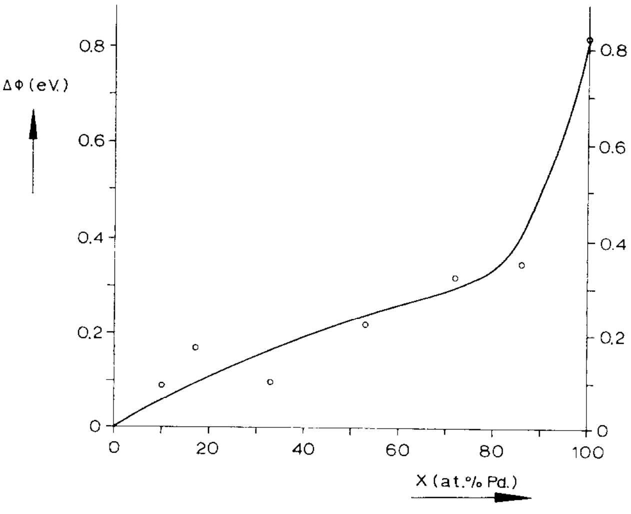

FIG. 6. Change of the work function of Ag–Pd alloy films caused by CO chemisorption as a function of the overall composition.

law [see, for instance, Ref. (*18*)], the X-ray diffraction method enables the bulk composition of the films to be determined provided that the alloy films are properly equilibrated. The bulk compositions of our films as derived from the lattice parameters agreed within 5% with the compositions as calculated from the weight loss of the filaments and the geometric setup of evaporation sources and cathode support.

3.3. *Chemisorption-Induced Aggregation of the Alloy Surfaces Under Influence of CO at 293, 373, and 441 K*

After exposure of the films to 1.3 × 10^{-2}N m^{-2} CO during several hours at room temperature, the work function of all alloys, with exception of the Ag-rich alloys, had increased. This effect, which is enhanced by heating the film at 373 and 441 K, respectively, in the presence of CO increases with the Pd content of the film (Fig. 4). The emission data from Ag-rich compositions yield single linearized Fowler plots but those from Pd-rich alloys yield composite Fowler plots. For the latter the lower value Φ_1 is equal ($\Phi_1 = 4.51 \pm 0.01$ eV) for all compositions and pure Pd, irrespective of the treatments to which the film was subjected; whereas the difference between the two characteristic threshold frequencies rises with increasing Pd content and with prolonged CO treatment (Fig. 7). It is noteworthy that the composite Fowler plots are obtained only after prolonged treatment with CO; whereas the initial curves are single straight lines. The emission constant of Pd-rich films is further reduced substantially after prolonged treatment with CO at 373 K. The change in *M* for Ag-rich alloys is not appreciable and appears to give no systematic trends. After desorption by heating the film at 573 K while pumping, the original Φ versus x curve of the freshly equilibrated film is reclaimed, although CO is not removed completely from pure Pd. Most *M* values have increased to almost their original values prior to admission of CO (Fig. 8).

4. Discussion and Conclusions

Before touching the question of the surface composition of alloys, the emission behavior of pure Pd after chemisorption of CO is briefly discussed. The spectral distribution curve of the photoelectric

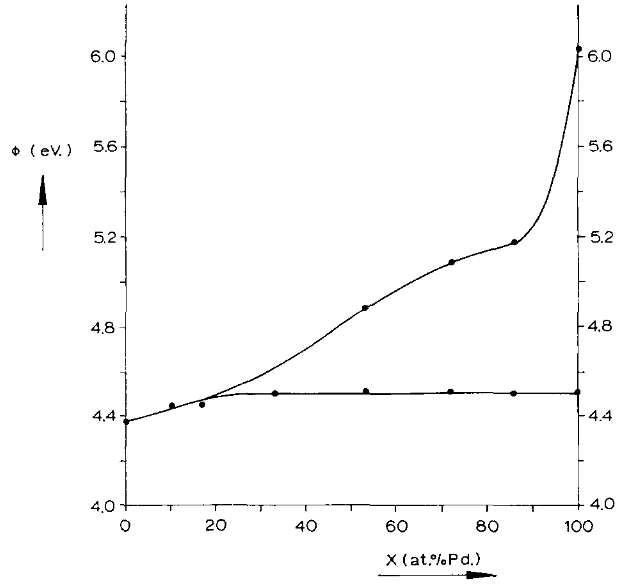

FIG. 7. The two work functions Φ_1 and Φ_2 of Ag–Pd alloy films treated during 16 hr with CO ($p = 1.3 \times 10^{-2}$ N m^{-2}) at 373 K.

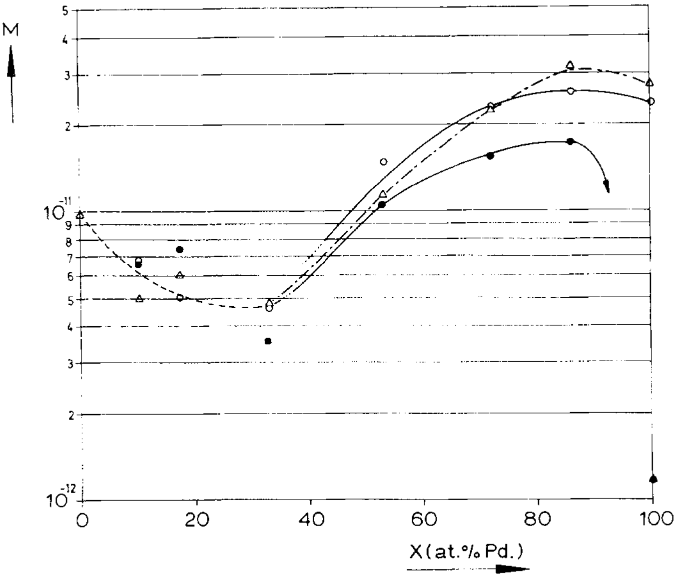

FIG. 8. The emission constant of Ag–Pd films as a function of the overall composition before and after desorption of CO: (△) freshly equilibrated film; (●) after 16 hr exposure to 1.3×10^{-2} N m^{-2} CO at 373 K; (○) after desorption of CO at 573 K.

yield of the CO-covered Pd is puzzling. To our knowledge no data of this kind have ever been reported for any group VIII metal covered with CO. Similar composite plots have, however, been found by Anderson and Klemperer (*19*) for Ni + O_2 and by Suhrmann *et al.* (*20*) for Bi + O_2. The results on the latter systems could be interpreted as having been caused by a semiconducting surface layer [see also Ref. (*21*)]. We strongly doubt that this interpretation could be applied to CO-covered Pd. When analyzing our data according to any of Kane's plotting methods (*22*), it appears that the spectral distribution of the photoelectric yield bears no relationship with any of the known types of semiconductors. Another explanation might be considered in which CO is chemisorbed in such a way that it yields electronegative ad-species on closely packed crystal planes (which, after equilibration of the film at 573 K, can be expected to prevail in the surface) whereas it yields electropositive ad-species on other atomically rough planes due to, for instance, corrosive chemisorption. This model leads to a series of patches showing considerably different electrostatic double layers. If these patches are sufficiently large, electrons can be emitted independently from each patch giving rise to the appearance of two threshold quantities Φ_1 and Φ_2. This hypothesis is, in principle, in agreement with our previous findings on the Pt + CO system (*11*) for which two ad-species having opposite dipoles were detected. For this system the electropositive adsorbate (which lowers the work function) appears with preference on disordered films and vanishes with increasing ordering of the film. As it seems that the heat of adsorption of CO on Pd is higher than that of CO on Pt, while the heat of sublimation of Pd is lower than that of Pt, it is likely that CO is able to induce surface aggregation more vigorously on Pd than on Pt.

Although the change of Φ_{Pd} by adsorbed CO is thus more complicated than in the case of, say, Ru (*23*), there is a fair indication that the highest work function ($\Phi_2 = 6.04$ eV) can be regarded as a "fingerprint" for Pd present in the surface of the alloys. This follows from the data in Fig. 7 which show that the lower work function Φ_1 is constant ($\Phi_1 = 4.51 \pm 0.01$ eV) for *all* alloys with composite Fowler plots, but the higher work function Φ_2 increases for Pd-rich alloys with the Pd content. The $\Delta\Phi_2$ value being +0.84 eV is in reasonable agreement with values found for single crystals [+0.98 eV for Pd (111) (*24*) and 0.75 eV for Pd (100) (*25–27*)]. Evidently, Φ_2 is qualitatively indicative for the Pd content of the surface but we do not see a possibility to calculate quantitatively the surface composition from the observed $\Delta\Phi$ values.

Two important implications with respect to the surface titration of Pd atoms in an Ag–Pd surface matrix are: (a) the heat of adsorption on these alloys; and (b) the possible presence of linear and/or bridged CO-adsorption complexes.

With regard to the first question, it cannot be excluded that the heat of adsorption of CO on a Pd atom which is completely hemmed in by Ag atoms might be too low for any appreciable adsorption at the low pressures used in this work. The lower heat of adsorption of CO on the alloys is qualitatively demonstrated by the desorption experiments (see Table 1). After desorption of CO from the film at 573 K all original Φ values of the alloys are reclaimed with the exception of that of pure Pd. Recent values (*28, 29*) of the isosteric heats of adsorption of CO on pure Pd at low coverage are 34 kcal mole^{-1} for the (100) plane and about 40 kcal mole^{-1} for the (110) plane. It is not unlikely that a small proportion of CO corresponding with a $\Delta\Phi$ value of about 0.1 eV remains bound by the less closely packed crystal planes after desorption at 573 K. Regarding the second question, it is well known from the chemistry of group VIII metal carbonyls that strong metal–CO bonds can be formed both in linear and bridged structures. We therefore consider isolated Pd atoms in a silver matrix capable of forming a linear adsorption complex.

Bearing these limitations in mind, the problem of the determination of surface composition of alloys prior to and immediately after adsorption of CO will be discussed. For a description of the phenomena involved, we shall first use the idealizing assumption that every Pd atom in the surface is capable of adsorbing CO and that the effective dipole moment of the adsorption complex in the absence of other adsorbed molecules is virtually independent of the nature of the surrounding metal atoms. On basis of these assumptions the $\Delta\Phi$ versus x curve of the initial CO adsorption experiments should have the shape of one of the curves presented in Fig. 9:

1. A straight line connecting the experimentally obtained values $(\Delta\Phi)_{Ag} = 0.00$ eV with $(\Delta\Phi)_{Pd} = 0.84$ eV (curve I). This can

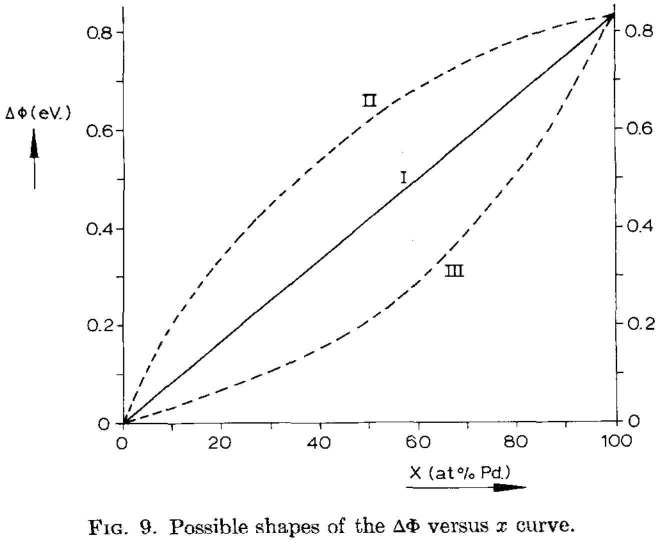

FIG. 9. Possible shapes of the $\Delta\Phi$ versus x curve.

be expected if the surface composition is equal to that of the bulk and if there is no mutual depolarization between the adsorbed CO-dipoles.

2. Curve II (above curve I) connecting the same experimental points will be obtained if the surface is enriched with Pd or if the surface composition is about equal to that of the bulk but mutual depolarization occurs between the adsorbed CO dipoles at higher degrees of coverage.

3. Curve III below curve I is expected for the case that the surface is enriched with Ag.

The experimental results clearly follow a curve of type III so that we may conclude that the surface is enriched with Ag. This was, in principle, to be expected on basis of thermodynamics. Ag possesses the lower heat of sublimation and therefore the lower surface energy. According to Semenchenko (*30*) the surface energy of Ag at 995°C is 927 erg/cm^2; while for Pd, no experimental data being known, a value of 1190 erg/cm^2 is calculated from Zadumkin's formula. The results presented in Fig. 6 also demonstrate that, in contrast to the Cu–Ni and Au–Pt alloys, the surface composition of Ag–Pd changes gradually with that of the bulk in agreement with the expectation for a single-phase alloy. There are two other arguments which support our belief that the clean alloy surfaces are enriched with Ag:

1. The work function of the clean equilibrated alloys are low and roughly equal to Φ_{Ag}. (However, this observation alone would not be conclusive in view of the fact that the work function of alloys when plotted versus the composition shows in some cases a minimum (*1*, *2*, *10*) so that a linear interpolation between the work function of the pure metals is a priori not justified.)

2. Immediately after admission of CO (see Table I) single linearized Fowler plots are obtained for all alloys, while a composite plot is obtained only for Pd. After rigorous treatment with CO the enrichment of the surface with Pd yields composite Fowler plots (see below). The absence of this phenomenon immediately after adsorption seems to indicate a low Pd content of the alloy surfaces in this stage.

The last point to be discussed concerns the phenomenon of chemisorption-induced aggregation. The present results appear quite conclusive in this respect. They are even more so than those with the Au–Pt alloys. Probably the higher mobility of Pd atoms compared with Pt explains this difference.

The process of chemisorption-induced aggregation proceeds with the highest rates for Pd-rich alloys just as observed for Pt-rich alloys in the case of Au–Pt. It is unknown whether chemisorption induced aggregation of the Ag–Pd alloys proceeds by the creation of vacancies in and below the surface of the film as a consequence of corrosive chemisorption of CO. The appearance of two threshold quantities Φ_1 and Φ_2 for CO-covered Pd and Pd-rich alloys of which the first quantity Φ_1 can be ascribed to corrosive chemisorption might serve as a support for the proposed model of the chemisorption-induced aggregation. For Ag–Pd, however, this needs not to be a condition sine qua non because the enhanced mobility of Ag and Pd atoms at 373 K (*31*) could account for rapid aggregation effects also in the absence of corrosive chemisorption. The resemblance of this effect in Au–Pt and Ag–Pd is also illustrated by the similar behavior of the emission constants in both systems. The M values prove in particular the reversibility of the surface aggregation phenomena upon removing the adsorbate.

Chemisorption-induced aggregation was also invoked in recent papers by Moss and Thomas (*32*, *33*) to explain an enrichment with Ag of Ag–Pd surfaces in contact with gaseous oxygen. Unfortunately, that case is less clear-cut than the system studied in the present work, as oxygen is able to form strong bonds with both Pd and Ag atoms. Due to the extraordinary wide scatter of literature data on the heat of oxygen adsorption on silver (*34*), it is debatable whether thermodynamics favor an enrichment of the surface with silver. A value of 108 kcal mole^{-1} has been reported by Bortner and Parraveno (*18*) for oxygen coverages on silver of 10^{-4}–10^{-3}, while the same authors observe only a value of 49.2 kcal mole^{-1} for oxygen on palladium at similarly low coverages. Ostrovskii and Temkin (*35*) find that the heat of adsorption on silver decreases with coverage from 130 to 10 kcal mole^{-1}. It appears, however, that the majority of investigators find for Ag + O_2 values below those for Pd + O_2. Published data for Ag + O_2 are, e.g., 16 kcal mole^{-1} [Benton and Drake (*36*)], 17–25 kcal mole^{-1} [Smeltzer *et al.* (*37*)], 18–19 kcal mole^{-1} [McCarty (*38*)], and 16 kcal mole^{-1} [Sandler *et al.* (*39*)]. Also the measured data on the activation energy of desorption, viz., 32.5 kcal mole^{-1} [Sandler and Durigon (*39*)] and $>$ 25 kcal mole^{-1} [Czanderna (*40*)] are consistent only with relatively small heats of adsorption although they do not necessarily exclude that very small quantities of oxygen might be too strongly bound to be desorbed. The published values of the heat of adsorption of Pd + O_2 are larger, e.g., 67 kcal mole^{-1} [Brennan *et al.* (*41*)] and 48–80 kcal mole^{-1} for Pd (110) [Ertl and Rau (*28*)]. A higher heat of adsorption for Pd + O_2 than for Ag + O_2 would be in line also with the heats of formation of the two parent oxides (*42*), i.e., 20.4 kcal mole^{-1} for PdO but 6.3 kcal mole^{-1} for Ag_2O.

A similar problem arises when the data by Jamin-Changeart and Talbot-Besnard (*43*) are discussed who observed surface aggregation effects of Ni–Fe alloys at 850°C in the presence of H_2S, the surface becoming enriched with Ni. Here again, the direction of the aggregation cannot easily be predicted on the basis of enthalpy data which seem to favor iron sulfide over nickel sulfide. Still, the experimental data of these authors prove the reality of the phenomenon of chemisorption-induced aggregation. It implies a serious consequence for catalysis by alloys. Until recently, most authors on this subject had tacitly assumed that the surface composition of alloys remained unaltered in the course of a catalytic reaction. Our results on the Au–Pt and Ag–Pd system demonstrate, however, that in the steady state of a catalytic reaction the alloy catalyst will adapt its surface composition to the thermodynamic requirements of the ambient atmosphere.

It is a point of discussion whether this steady state is always established within the periods of laboratory experiments, but for commercial catalysts, usually operative for several years the steady-state conditions will, in general, be obtained. The same catalyst then exposes different surfaces to different reacting gases.

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